1. Introduction

Three-dimensional (3D) nanostructure materials are those materials that have three dimensions outside nanoscale but with nanometer-sized features in all directions, and are spatial organizations constructed using zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) nanostructures [1,2]. 3D nanostructures can be arrayed as 1D/2D nanostructures [Fig. 1(a)–(c)], 3D nanoporous structures [Fig. 1(d)–(e)], or 3D hierarchical nanostructures [Fig. 1(f)] [3]. Owing to their unique mechanical, electrical, thermal, and optical properties arising due to size effects brought by the constituent nanostructures and abundant active catalytic/reactive sites due to larger surface area and overall size than the 0D, 1D, and 2D constituent nanostructures, 3D architectures with well-tailored nanostructures have been widely studied for potential applications in diverse fields [3–5]. Various 3D nanoscale structures have been reported for environmental greening [Fig. 2(a)] [6], sustainable energy conversion and storage [Fig. 2(b)] [7], biomedical [Fig. 2(c)] [8], and optical applications [Fig. 2(d)] [9]. 3D nanofabrication comprises the design and manufacturing of 3D nanostructures with a relatively high degree of functionality, structural complexity, and hierarchy. These techniques can be broadly classified into top-down approaches and bottom-up approaches (Fig. 3) [10–12].

Recent years have witnessed a rapid expansion of research on advanced nanotechnologies for 3D nanofabrication. In top-down approaches, various nanolithography techniques, such as optical lithography, electron-beam lithography (EBL), interference lithography (IL), direct laser writing (DLW), nanoimprint lithography (NIL), and 3D nanoprinting methods (such as focused electron beam (FEB)-induced deposition, focused ion beam (FIB)-induced deposition, and direct ink writing (DIW)) have been employed to create a variety of 3D nanogeometries [13]. In bottom-up approaches, self-assembly has been extensively used to fabricate versatile 3D geometries [14]. Each of these techniques has demonstrated distinct advantages and revealed enormous potential for the fabrication of various classes of nanostructures and devices. Nevertheless, none provides a complete solution to the challenge of 3D nanofabrication, due to various combinations of disadvantages that include limited flexibility in the structure geometries, slow speeds, applicability only to relatively small areas, complex experimental setups, and uncertain yields and defect densities [15]. This review provides a comprehensive overview of advanced fabrication technologies and processes currently available to generate 3D nanostructures and discusses their general advantages, existing challenges, and future prospects.
2. Top-Down Techniques

2.1. Nanolithography

Lithography is a process used to generate nanoscale structures on substrates by first creating a pattern in the resist that covered the substrate and then transferred it to the substrate by etching or lift-off [16]. Diverse lithographic patterning techniques, such as optical lithography, IL, EBL, DLW, and NIL have been widely employed to fabricate functional 3D nanostructures and systems [17].

Optical lithography (also known as photolithography) such as ultraviolet (UV) lithography and X-ray lithography are mask-required semiconductor device fabrication methods used to create 2D and 3D on the surfaces of semiconductor materials. These two methods first use UV light or X-rays to transfer a geometric pattern from a mask to a light-sensitive chemical photoresist on the substrate. A series of chemical treatments then is used to etch the exposure pattern into the material or enables deposition of a new material in the desired pattern upon the material underneath the photoresist. The process for these two methods generally contains several steps (Fig. 4) [18]. Optical lithography has been successfully employed to create 2D nanopattern layers. However, 3D nanofabrication needs to be achieved by stacking those layers. A set of different masks is required to form each of those different layers through overlay alignment. Furthermore, precise optical systems with vertical and horizontal steppers are required for repositioning and registration. Therefore, the overall procedure is tedious, expensive, and difficult to master [19,20].

EBL, DLW, and IL are maskless lithography methods following a process similar to mask-required lithography, except that patterns are transferred onto substrates without utilizing an intermediate mask [13].
Figure 3. Top-down and bottom-up approaches of 3D nanofabrication. (Reproduced from [12]. CC BY 3.0.).

Figure 4. Processing steps in optical lithography using positive and negative resists. (Reproduced from [18]. CC BY 3.0.).
EBL is one of the most important nanofabrication methods and is generally used by directly illuminating a high-voltage electron beam onto an electron-sensitive resist to create desired patterns down to a few nanometers [Fig. 5(a)]. However, EBL is also a 2D method [19,21]. There are two strategies to apply EBL to 3D nanofabrication. One is the complex and time-consuming layer-by-layer stacking. The other one is using conformable elastomeric phase masks [22].

DLW, also known as multiphoton lithography or direct laser lithography, is a laser-assisted fabrication technique performed by scanning a tightly focused laser beam according to designed patterns into a photosensitive material (photoresist) to form 3D structures with complex shapes and self-supporting features at resolutions down to tens of nanometers [Fig. 5(b)] [23]. 3D nanostructures formed in this way rely on polymerization of specialized polymers via two- or multiphoton absorption. The formed photoresist with 3D nanopatterning then serves as a sacrificial template for forming structures in metals, ceramics, and other materials through conformal deposition and selective removal of the polymer [24]. Currently, UV, nanosecond pulsed, excimer, and Nd:YAG are the most commonly used lasers. However, shorter pulse lasers, such as picosecond and femtosecond lasers, are also finding application as precision writing tools [25,26]. Although DLW also shares the drawbacks of being time-consuming and having low throughput and high cost, it has been intensively exploited to fabricate various arbitrary 3D nanostructures (Fig. 6) [27].

IL, also known as holographic lithography, utilizes the interference of coherent beams of lights to create 1D, 2D, and 3D periodic patterns (Fig. 7) [28,29]. IL can create 3D nanoscale features without the use of complex optical systems, photomasks or conventional layer-by-layer stacking processes. IL provides access to various 3D nanostructures by altering the number of interfering beams, wave vectors, and phases. It allows rapid creation of large 3D nanostructures [30,31]. There are two broad approaches currently employed to yield 3D interference patterns: phase mask IL and multibeam IL [31,32]. However, IL suffers from index mismatching between the polymer and substrate, limited availability of space to arrange multiple beams, and registration problems. Solutions such as the use of phase shift mask and translational stages and multiple exposures have been employed to address these challenges [30]. Researchers also explore the possibility to integrate multibeam IL and two-photon/multiphoton lithography
to enable fast production of 3D structures with controlled and functional elements [27].

NIL relies on direct mechanical deformation of imprint resist and subsequent processes to create patterns [33]. In the NIL process, a prefabricated mold containing an inverse of the desired patterns is first pressed onto a resist-coated substrate to replicate the patterns via mechanical deformation. Then a similar pattern transfer process, including etching and lift-off, can be used to transfer the pattern in resist onto the substrate [34]. In terms of resist curing, there are two fundamental types of processes: thermal NIL and UV NIL (Fig. 8) [35]. Since NIL replicates the nanopattern of the mold regardless of the diffraction limit set by light or beam scattering factors as observed in conventional nanolithography methods, it can achieve sufficiently high productivity and patterning resolution at low cost [36]. A large volume of studies exist in the literature that have explored NIL-based technology for creating 3D nanoscale structures (Fig. 9) using various promising materials [37–41]. The NIL process carries simplicity, low cost and high throughput. Besides, the roll-to-roll-based NIL process shows a highly promising future to be implemented as a full-scale production process for various applications due to their high throughput and wide-area patterning capability [42].

Comparative analysis of various nanolithography methods is provided in Table 1.

Figure 6. (a) Lattice structure base elements: nonlinear thrust, octet, and hex structure (left to right), SEM image of (b) nonlinear thrust, (c) octet, and (d) hex structure. (Reproduced from [27]. CC BY 4.0.).
2.2. 3D Nanoprinting Techniques

3D printing is an additive manufacturing method to produce high-aspect-ratio 3D structures in a layer-by-layer manner without any additional process steps [43]. Recent efforts on nanoscale 3D printing have provided an innovative series of tools for direct fabrication of 3D nanostructures. Some of the mentioned techniques directly transferring nanoparticles to the substrate include focused electron-beam-induced deposition, focused ion-beam-induced deposition, and DIW [44,45].

Focused electron-beam-induced deposition (FEBID) is an additive, direct-write approach for synthesis of 3D architectures on complex substrate topographies without the need of masks, resists, etching, or lift-off processes and is made possible by the scanning or transmission electron microscope (SEM/TEM) platform [45]. In FEBID, injected gaseous precursor molecules are absorbed onto the sample surface and then dissociated by incident energetic electrons, leading to the formation of a solid deposit (Fig. 10) [46]. The composition and the short-range atomic order of the condensed molecular aggregate is a function of both the concentration of precursor molecules and the electron beam parameters such as beam accelerating voltage, current density, and dose. FEBID allows fabrication of highly complicated 3D geometries with nanometer resolution on morphologically challenging substrates as well as flexibility in structural design and material choice, as the adsorption of the precursor gas is not limited to flat surfaces and the position/movement of the electron beam can be easily controlled in a well-defined manner [47,48]. One main issue of FEBID is low speed and throughput when performed on single-electron beam machines. However, multibeam FEBID with 196 beams in one microscope was demonstrated, as well as FEB and FIB microscopes with >10⁵ individually addressed beams, would allow boosting the overall speed accordingly (for 1000 beams) [49]. The other main issue of FEBID is the existence of chemical impurities due to incompletely dissociated precursor molecules, leading to incorporation of unwanted fragments inside deposit, often containing C and O [50]. Various post-growth purification strategies have been developed to improve the deposit purity. Due to these advantages of FEBID, in conjunction with the ever-growing reservoir of suitable precursors for a wide range of material properties of the deposits and the development of purification strategies and advanced gas injection systems (GISs), FEBID offers a roadmap to high-quality, multicomponent materials.

Figure 8. Comparison of a typical thermal NIL and UV NIL process (Reproduced from [35]. CC BY 4.0.).
Figure 9. 3D nanoscale structures fabricated by NIL. (a) Large-area nanogap-controlled 3D nanoarchitectures (Reproduced with permission [37]. Copyright 2021, American Chemical Society); (b) GaN nanorods with axial InGaN/GaN quantum well insertions (Reproduced from [38]. CC BY 4.0.); (c) silver gratings (Reproduced from [39]. CC BY 4.0.); (d) multifunctional nanoprobes (Reproduced from [40]. CC BY 4.0.); (e) nanopillar structures (Reproduced from [41]. CC BY 4.0.).
Figure 10. Illustration of FEBID. Precursor molecules (here: organometallic complex; blue, metal; green, organic ligands) are supplied by a gas-injection system and physisorb (1) on the surface. Surface diffusion (2), thermally induced desorption (3) and electron-stimulated desorption (3') take place. Within the focus of the electron beam, adsorbed precursor molecules are (partly) dissociated followed by desorption of volatile organic ligands (4). Upper right: For pattern definition, the electron beam is moved in a raster fashion (here, serpentine) over the surface and settles on each dwell point for a specified dwell time. After one raster sequence is completed, the process is repeated until a predefined number of repeated loops is reached. (Reproduced from [46]. CC BY 2.0.).

Figure 11. 3D nanoscale structures fabricated by FEBID. (a) “Calla lily flower petals,” an array of identical concentric bows; (b) Moebius strip with triangular cross section and individual wire dimensions around 25 nm (Reproduced from [45]. CC BY 4.0.).
<table>
<thead>
<tr>
<th>Nanolithography Method</th>
<th>Lithography Mechanism</th>
<th>Resolution</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV lithography</td>
<td>Transfer a pattern from a mask to a surface using UV light</td>
<td>~ 100 nm</td>
<td>Cheap</td>
<td>Limited by UV wavelength and mask</td>
<td>18–20</td>
</tr>
<tr>
<td>X–ray lithography</td>
<td>Transfer a pattern from a mask to a surface using X–ray</td>
<td>~ 15 nm</td>
<td>Accurate, efficient fast</td>
<td>Expensive; masks are fragile</td>
<td>18–20</td>
</tr>
<tr>
<td>EBL</td>
<td>Transfer a pattern onto the surface of a substrate by first scanning a thin layer of organic film (called resist) on the surface by electron beam (exposure) and then selectively removing the exposed or nonexposed regions of the resist in a solvent (developing)</td>
<td>&lt; 10 nm</td>
<td>Highly accurate; can print complex computer generated patterns directly on the wafer; can work with a variety of materials and an almost infinite number of patterns</td>
<td>Very expensive and complex with high maintenance cost; forward scattering and back scattering problems; slower speed</td>
<td>13,19,21,22</td>
</tr>
<tr>
<td>DLW</td>
<td>Scan a tightly focused laser beam according to designed patterns into a photosensitive material</td>
<td>~ 50 nm</td>
<td>No need of mask, easy to operate, can design and print complicated 3D structures in a straightforward manner</td>
<td>Limited by working field; time-consuming; low throughput; high cost</td>
<td>23–27</td>
</tr>
<tr>
<td>IL</td>
<td>Optical beams interfere in a 3D volume, resulting in the capability to pattern nonflat surfaces</td>
<td>&lt; 10 nm</td>
<td>Quick generation of dense features over a wide area without loss of focus</td>
<td>Limited to patterning arrayed features or uniformly distributed aperiodic patterns only</td>
<td>27–32</td>
</tr>
<tr>
<td>NIL</td>
<td>Use of a mold to define nanoscale deformation of a resist, which is then cured either by heat or UV application</td>
<td>&lt; 10 nm</td>
<td>Mass production capability</td>
<td>Limited by organic polymer’s optical and mechanical properties, such as transparency and thermal stability</td>
<td>33–42</td>
</tr>
</tbody>
</table>
Focused ion-beam-induced deposition (FIBID) is a direct-write 3D nanofabrication technique similar to FEBID. The difference is that instead of using a focused electron beam as the writing tool, FIBID uses a closely focused beam of positively charged ions to direct write 3D nano–objects [48]. During the FIBID process, the FIB breaks the gas precursor molecules coming from the GIS and leaves a deposit on the substrate, acting as a nucleation site for the nanostructure growth. The morphology of the deposition structure depends on the process parameters, which impose influence on the incident ion flux and the precursor gas distribution. The incident ion flux is determined by the beam current and optical lens assembled in the machine. The variation of precursor gas concentration is dependent on processing time and determined by adsorption, diffusion, decomposition, and desorption [51,52]. The most used ions are gallium (Ga⁺) ions generated by the liquid metal Ga⁺ ion source. In general, Ga⁺ ions can achieve ~10 nm practical beam resolution, but the scattered Ga⁺ ions stain the near surface region of the substrate/growing material [48,53]. Alternative light ions such as helium (He) and neon (Ne) ions based on gas field-ionization sources have also been developed and are currently being studied [54,55]. Compared with the Ga⁺ ions, He ions and Ne ions can manufacture cleaner 3D structures with higher theoretical resolution (He ions < 1 nm, Ne ions 1 nm). Since FIBID is based on the same principle of charged particle-beam-induced deposition as FEBID, it also shares the same advantages of high spatial resolution and flexibility regarding structural design of arbitrary complicated structures on virtually any surface and material choice. Besides these advantages shared with FEBID, FIBID has higher growth rates and deposit purity, increased electrical conductivity, and different functionalities (such as superconductivity) in comparison with FEBID [56]. Due to these advantages, FIBID has been widely used in circuit edit, mask repair, the construction of nanoactuators, nanosensors, and nanoelectrodes [53]. However, in sharp contrast with

Figure 12. Illustration of (a) continuous filament writing (Reproduced from [58]. CC BY 4.0.); (b) droplet jetting (Reproduced from [58]. CC BY 4.0.); (c) aerosol jetting (Reproduced from [60]. CC BY 3.0.).
FEBID, substantial beam-induced damage on the substrate (amorphization, implantation, defects, etc.) has been observed for FIBID, which can be detrimental in some cases [56]. Despite this, such “undesirable” defects have recently been utilized to develop a novel nanofabrication method (i.e., FIB nano–kirigami) to manufacture functional nanostructures and devices [48].

DIW is an extrusion-based printing technique to create arbitrary 3D shapes through the layer-by-layer deposition of printable inks. During the printing process, the ink with appropriate rheological properties is extruded from a fine nozzle and deposited on a substrate to form preprogrammed architecture [57]. Two types of ink media, liquid ink and aerosol ink, are used in the DIW technique. Liquid ink-based DIW can be divided into continuous filament-based approaches [Fig. 12(a)] and discontinuous droplet-based approaches [Fig. 12(b)] [58]. For continuous filament writing (such as robotic deposition, pen writing, and fused deposition), the inks are continuously extruding from a nozzle and the filament element is patterned on a fixed platform to construct the objects. Droplet-based writing (such as ink jet printing, and hot melt printing) allows the ink to inject drop-by-drop on demand. Among liquid ink-based DIW techniques, fountain pen and dip-pen writing has been utilized to generate nanopatterns straight to the substrates with a variety of ink options [44]. Aerosol ink-based DIW is an emerging contactless direct write approach for the production of arbitrary 3D structures using functional nanomaterial inks. In aerosol ink-based DIW, a functional ink is aerosolized and deposited to the substrate by a carrier gas [Fig. 12(c)] [59,60]. All DLW technologies offer the materials flexibility, high scalability, low cost, and ability to construct complex shape and multi-material structures by using multiple extrusion nozzles. Diverse ink-materials including ceramics, metal alloys, polymers, food, biomaterials, colloidal gels, hydrogels, and electronically functional materials have been used for 3D printing [61]. In contrast to liquid ink-based DIW, aerosol ink-based DIW allows the patterning of more complex surfaces and the use of 3D nonplanar substrates [62]. Despite these potential advantages, some issues like structural distortion and defects at corner for liquid ink-based DIW and overspray for aerosol ink-based DIW still need to be faced [63].

Comparative analysis of various 3D nanoprinting methods is provided in Table 2.

### 2.3. Nanomachining

Nanomachining is a subtractive manufacturing method to produce structures with nanometer accuracy by removal of materials. Nanomachining technologies such as laser beam machining (LBM), tip-based nanomachining (TBN), and FIB milling have been explored for fabrication of complex 3D nanostructures made of different materials [64–66].

LBM is a noncontact machining technology that uses high-intensity laser beams to cut or ablate materials (Fig. 13) [67]. High frequency of monochromatic light falls on the surface, heats, melts, and vaporizes the materials. LBM is a versatile process that can shape a broad range of materials such as...

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**Table 2** Comparative study of different 3D nanoprinting methods

<table>
<thead>
<tr>
<th>3D Nanoprinting Method</th>
<th>3D Nanoprinting mechanism</th>
<th>Resolution</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEBID</td>
<td>Create metal-containing nanostructures by using electrons to induce local decomposition of organometallic precursors adsorbed on solid substrates in a vacuum environment</td>
<td>&lt; 10 nm</td>
<td>Very flexible regarding deposit shape and composition; the deposited material can be characterized using electron microscopy techniques</td>
<td>Limit throughput and mass production (such as C and O); hard to control the chemical deposit composition</td>
<td>45–50</td>
</tr>
<tr>
<td>FIBID</td>
<td>Create metal-containing nanostructures by using ions to induce local decomposition of organometallic precursors adsorbed on solid substrates in a vacuum environment</td>
<td>&lt; 10 nm</td>
<td>Besides the same advantages as FEBID, FIBID has higher growth rates and deposit purity, increased electrical conductivity, and different functionalities than FEBID</td>
<td>Lower spatial resolution; Ga+ ions introduce additional contamination and radiation damage to the deposited structure</td>
<td>48.5–1–66</td>
</tr>
<tr>
<td>DIW</td>
<td>Create metal-containing nanostructures by using liquid phase “ink” dispensed out of small nozzles under controlled flow rates and deposited along digitally defined paths to fabricate 3D structures layer by layer</td>
<td>&gt; 100 nm</td>
<td>Design freedom, low-quality control, economy, material efficiency, reduced assembly, and predictable production</td>
<td>Limited materials, restricted build size, process dependent on slow mass production</td>
<td>44,57–63</td>
</tr>
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metals, polymers, glasses, ceramics, and composite materials. And different types of laser machining systems have been applied for these varieties of materials where complex shapes demand precise, fast, and force–free processing [68,69]. For example, a CO$_2$-based laser beam has been attempted to analyze the effects of process parameters on the surface performance of the titanium alloy [70]. The femtosecond laser has been studied to fabricate high hardness microarray diamond tools [68]. The picosecond laser has been used to produce smooth, deep and defect-free cuts of desired geometries on alumina ceramics with a high degree of precision [71]. The nanosecond laser has been utilized to ablate SiCp/AA2024 composites with increased ablation depth and rate [72]. These developed laser systems have been utilized for fabricating engineered net-shaping material systems for applications including bio-inspired architectured materials, interlocking sutures, topologically interlocked ceramics, semiconductors, electronics, surface treatments, multilayer ceramic packaging for microelectronics, scribing engineering, and laser surface cleaning [71]. In general, LBM is a powerful machining method for cutting complex profiles and drilling holes in wide range of workpiece materials. Machining accuracy and surface quality depend on the process parameters and the composition and initial surface finish. However, the main disadvantages of this process are low energy efficiency from a production rate point of view and converging diverging shape of beam profile from the quality and accuracy point, low resolution limited to micrometers, and surface damage [68].

TBN has emerged from the well-established scanning probe microscopy (SPM) platform to manufacture nanointegrated systems of the second and third generations. In TBN, a nanoscale tip is brought into close proximity or contact with a substrate to modify the surface using thermal, mechanical, or electrical fields. In particular, it delivers capabilities for higher resolution (< 20 nm) manufacturing with process flexibility, integrated processing, assembly, metrology, and visualization in a cluster tool through the use of different nanoscale tool tips. TBN techniques can be categorized by the instrumentation platform to be scanning tunneling microscopy (STM), atomic force microscopy (AFM), and nanoindenter-based TBN [73,74]. In AFM tip-based TBN method, the AFM probe tip is employed as a nanocutting tool in the machining process, as shown in Fig. 14 [75]. Currently, the AFM probe tip method is known to be a low-cost, simple, highly accurate, and flexible method, and is widely employed in many research fields to machine nanoscale features [76]. For example, AFM-based 3D nanofabrication assisted using ultrasonic vibration has been reported to fabricate a set of 3D nanostructures on polymethyl methacrylate (PMMA) samples [73]. A modified AFM TBN

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Figure 13. LBM setup (Reproduced from [67]. CC BY 3.0.)
SEM uses a focused beam of electrons to image the sample. However, FIB uses a finely focused beam of ions (usually Ga⁺) that can be operated at high beam currents for site-specific milling or at low beam currents for imaging. FIB can also be incorporated in a system with both SEM and ion beam columns, which is called dual-beam (also called two-beam or multibeam) platforms. Dual-beam platforms, additionally equipped with GIs and secondary electron (SE) detectors, can serve as multifunctional tools for the purpose of milling the sample surface and as a method of imaging (Fig. 15) [78]. During the process, the ion beam locally scans the surface, digging the targeted area. The sputtering rate is ruled by the energy of the beam, which hits and locally removes the substrate atoms. During the sputtering removal, the ions are implanted into the sample. FIB milling can fabricate complex microfeatures with enhanced throughput has been developed by combining fast reciprocating motions of a shear-type piezoelectric actuator and linear displacements of the AFM stage [77]. To date, nanodots, lines/grooves, 2D/3D structures, and even nanostructures on curved surfaces have already been successfully obtained on different materials using the AFM TBN method. Despite these advantages, the AFM TBN method is not yet considered a serious competitor for nanoscale manufacturing. This is partly due to its small material removal rate and large setpoint force, which results in high tip wear rate, slow machining speed, and low throughput [77].

The FIB is a multifunctional tool that can inspect, cut, deposit, and touch a sample with nanoscale precision. It operates using a principle similar to a scanning electron microscope (SEM).

![Diagram](image_url)

**Figure 14.** (a) Illustration of AFM TBN; (b) example of a machined pocket with a step-over of 100 nm (Reproduced from [75]. CC BY 3.0.).
on nearly all workpiece materials with high surface quality and dimensional accuracy because of ultralow ion scattering effect. At present, FIB milling has become the method of choice in various applications, such as the circuit editing of semiconductor devices, cross-sectional materials analysis, and transmission electron microscopy samples preparation. FIB milling is also employed to fabricate high-quality and high-precision components for optical, mechanical, thermofluidic, and biochemical applications [79,80]. However, FIB milling is currently still limited to a micromachining method. The other fundamental feature that has so far hindered the widespread use of FIB milling in nanophotonics is the low purity level of the fabricated nanostructures [64]. During the milling process, the impurities introduced by the Ga$^+$ implantations and redeposition of the sputtered atoms can alter the fabricated nanostructure, damaging the substrate [48,56].

Comparative analysis of various nanomachining methods is provided in Table 3.

### 3. Bottom-Up Techniques

Self-assembly is an important bottom-up method to fabricate nanostructures. Self-assembly is a process in which the individual components such as atoms, molecules, or a collection of molecules organize themselves into ordered, functional ensembles without external intervention [81]. In the self-assembly process, various noncovalent intermolecular interactions such as van der Waals interaction, hydrophobic interaction, π–π stacking, hydrogen bonding, ion pairing, cation–π, anion–π, dipole–dipole, halogen bonding, and metal coordination interaction between disordered building blocks have been used to drive the system toward the formation of more ordered (or more organized) nanostructured systems (Fig. 16) [82].

Although most of the self-assembly is performed spontaneously, direct self-assembly is a more useful and controllable way to form 3D nanostructures with a more large-scale ordered and hierarchical pattern. Direct self-assembly is a self-assembly process driven by external factors. Different force fields such as gravity, centrifugal force, or electrostatic force, magnetic field, capillary force, light, ultrasound, and templates have been used to trigger or direct self-assembly [27,82]. A great variety of materials, including colloids, crystalline materials, block copolymers, peptides, and deoxyribonucleic acid (DNA) have been self-assembled into ordered nanostructures [81,82]. Metal oxide-based nanostructures, DNA-based nanostructures, and polymer-based nanostructures fabricated by self-assembly have found widespread applications in diverse fields [83]. For example, a 3D microstructure that contains in situ growth of the Ni(OH)$_2$ nanowalls at specific locations has been fabricated for use as wafer-scaled miniaturized gas sensors (Fig. 17), and 3D flower-like hierarchical nitrogen-doped and carbon-sensitized Nb$_2$O$_5$ (N–NBO/C) nanostructures have been fabricated for solar energy transformation and environmental remediation (Fig. 18) [84,85]. Despite this, the structural control over a larger scale range, mechanical properties of the self-assembly materials, the combination of different molecules into

<table>
<thead>
<tr>
<th>Nanomachining Method</th>
<th>Nanomachining Mechanism</th>
<th>Resolution</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBM</td>
<td>Use the thermal energy of the laser beams to cut or ablate materials</td>
<td>&lt;1 mm</td>
<td>Ease of automation for complex cutting patterns, absence of tool wear and breakage, ability to cut at shallow angles, and rapid cutting rates</td>
<td>Low energy efficiency, a relatively poor surface finish with damage (a recast layer on the as-machined surface), low resolution</td>
<td>67–72</td>
</tr>
<tr>
<td>TBN</td>
<td>Direct contact between the sharp tip of a probe and the surface of a sample in order to induce material removal or modification at very small scales</td>
<td>&lt;20 nm</td>
<td>Highly accurate</td>
<td>High tip wear rate, slow machining speed, and low throughput</td>
<td>73–77</td>
</tr>
<tr>
<td>FIB milling</td>
<td>Use a finely focused beam of ions (usually Ga$^+$) for site-specific sputtering or milling</td>
<td>&lt;10 nm</td>
<td>Highly accurate; can be combined with SEM and used for imaging, TEM preparation, transfer of sensitive samples, etc.</td>
<td>Ga$^+$ ions introduce additional contamination and radiation damage to the deposited structure</td>
<td>48,56,64,78–80</td>
</tr>
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</table>
advances have been achieved, as it is still in the early stages, several important issues, such as limited resolution, low throughput, high cost, limited flexibility in material choice, and 3D structure shape, still remain. Researchers must put more efforts into systematically developing 3D nanomanufacturing theory. From the perspective of 3D fabrication at nanoscale, future research can be conducted at an even smaller scale (atomic or close-to-atomic). To benefit from 3D nanostructured materials' advantages and to address their challenges, more intensive research needs to be conducted to develop ultraprecise nanofabrication methods, especially aimed at massive fabrication of 3D nanostructures at nanoscale resolution and low cost with excellent repeatability, controllability, and great flexibility. Moreover, the material behavior is critically important for 3D fabrication at nanoscale. New high-resolution testing methods should also be developed to comprehensively evaluate the 3D nanomanufacturing quality. Integrating is also an important trend (such as AFM TBN and dual-beam platforms) in developing 3D nanostructures. With the integrating established 3D nanomanufacturing methods, massive fabrication of high-resolution nanostructures will be realized.

4. Conclusions and Future Outlook

This study mainly surveyed the recent advancement in synthesis and fabrication for 3D nanostructured materials and summarized the general advantages as well as the existing challenges of each technique. Numerous top-down techniques have been implemented that have benefited the rapid development of 3D fabrication at nanoscale. The summarized features of lithography, 3D nanoprinting, and nanomachining processes that form nanosized structures from bulk materials are shown in Table 1 to Table 3, respectively. Bottom-up techniques based on self-assembly of molecules and particles driven by intermolecular interactions or external factors are also presented. The resulting 3D systems create interesting and unusual engineering design opportunities in cutting edge applications including biomedical, energy, optoelectronics, sensing, and device-based applications. Although many 3D nanofabrication methods have been successfully utilized to fabricate a variety of 3D nanostructures and considerable advances have been achieved, as it is still in the early stages, several important issues, such as limited resolution, low throughput, high cost, limited flexibility in material choice, and 3D structure shape, still remain. Researchers must put more efforts into systematically developing 3D nanomanufacturing theory. From the perspective of 3D fabrication at nanoscale, future research can be conducted at an even smaller scale (atomic or close-to-atomic). To benefit from 3D nanostructured materials' advantages and to address their challenges, more intensive research needs to be conducted to develop ultraprecise nanofabrication methods, especially aimed at massive fabrication of 3D nanostructures at nanoscale resolution and low cost with excellent repeatability, controllability, and great flexibility. Moreover, the material behavior is critically important for 3D fabrication at nanoscale. New high-resolution testing methods should also be developed to comprehensively evaluate the 3D nanomanufacturing quality. Integrating is also an important trend (such as AFM TBN and dual-beam platforms) in developing 3D nanostructures. With the integrating established 3D nanomanufacturing methods, massive fabrication of high-resolution nanostructures will be realized.

Figure 15. (a) Illustration of the specimen chamber of a dual-beam platform; (b) illustration of serial slicing and imaging application of dual-beam platforms. An ion beam is used for creating cross sections, while an electron beam allows for monitoring and imaging of the sliced regions. (c) Nanostructuring, nanofabrication, and maskless ion lithography examples performed by dual-beam instruments (Reproduced from [78]. CC BY 3.0.).
Figure 16. Scheme indicating the main stages of the self-assembly process (Reproduced from [81]. CC BY 4.0.).

Figure 17. (a) Schematic of fabricating wafer-scale miniaturized gas sensors; (b) dynamic response of eight gas sensors to different H₂S concentrations; (c) response of eight gas sensors toward different gases; the concentration is 5 ppm (Reproduced from [84]. CC BY 4.0.).
Figure 18. (a) Schematic for the formation of the flower-like hierarchical N–NBO/C nanostructures; (b) mechanism for photodegradation of Rhodamine B by N–NBO/C upon visible-light illumination (Reproduced from [85]. CC BY 4.0.).
Acknowledgments

This work is financially supported by the Natural Science Foundation (No. BK202001216), High Education Science Foundation (No. 21KJB540007), and Qinglan Project (No. Jiangsu Teacher 2022) of Jiangsu Province. The authors also acknowledge the financial support from the Open Project Program of Key Laboratory of Yarn Materials Forming and Composite Processing Technology (No. MTC2021–04), and the Jiaxing Public Welfare Technology Application Research Project (No. 2021AD10012) of Zhejiang Province. The authors are grateful for the Engineering Research Center for Clean Production of Textile Printing and Dyeing, Ministry of Education (No. FZYR 2021002 & FZYR 2021003) and the support from Jiangsu Province Engineering Research Center of Biomass Functional Textile Fiber Development and Application.

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